[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE IDENTIFICATION OF ACIDS. V. PARA HALOGEN PHENACYL ESTERS.

BY W. LEE JUDEFIND[1] AND E. EMMET REID.

Received February 26, 1920.

Introduction.

It has been shown by Rather and Reid[2] that phenacyl esters are in some cases superior to *p*-nitrobenzyl esters for the identification of acids, but in a number of cases the phenacyl esters are oils or low-melting solids. It is well known that *p*-nitro and *p*-bromophenyl hydrazones are sometimes solids when the unsubstituted hydrazones are oils. Previous work has shown that *p*-nitrobenzyl bromide is much more satisfactory than *p*-nitrobenzyl chloride on account of greater promptness and completeness of reaction with alkali salts. As *p*-nitro-acetophenone is not readily accessible, *p*-bromophenacyl bromide appeared to be the most promising reagent.

The results have confirmed this prediction. A number of *p*-bromophenacyl esters have been prepared and their properties studied. Partly for comparison, and partly to secure additional derivatives which might be of use in doubtful cases, some of the corresponding *p*-chloro- and *p*-iodophenacyl esters have also been studied.

Historical.

p-Chlorophenacyl bromide, $ClC_6H_4COCH_2Br$, or 4-chloro-1′bromo-acetophenone was made by Collet[3] by the Friedel and Craft reaction from monochlorobenzene and bromo-acetyl chloride. Later he prepared it by first making *p*-chloro-acetophenone[4] by the Friedel and Craft reaction and then brominating the methyl group. His product melted at 96–96.5°.

p-Bromophenacyl bromide, $BrC_6H_4COCH_2Br$, or 1′,4-dibromo-acetophenone, was also made by Collet by the same methods. The melting point, as observed by him, was 109–109.5°.

p-Iodophenacyl bromide, $IC_6H_4COCH_2Br$, is not described in the literature.

Of the *p*-halogenphenacyl alcohols, only the *p*-chlorophenacyl alcohol, $ClC_6H_4COCH_2OH$ (also known as *p*-chlorobenzoyl carbinol), is described in the literature. Straus[5] first made this compound from the acetate, which is also the only *p*-halogenphenacyl ester described. Upon boiling *p*-chlorophenacyl bromide in alcoholic solution with sodium acetate and a little acetic acid, he obtained the *p*-chlorophenacyl acetate which

[1] From a dissertation by W. Lee Judefind.

[2] THIS JOURNAL, 41, 75 (1919).

[3] *Compt. rend.*, 125, 717 (1897).

[4] *Bull. soc. chim.*, [3] 21, 69 (1899),

[5] *Ann.*, 393, 331 (1912).

melted at 65–66.5°. He then hydrolyzed the acetate by boiling it in water with barium carbonate. The alcohol crystallized out in needles melting at 122–3°.

Preparation of Reagents.

All 3 of the reagents were made by the second method used by Collet (*q. v.*). The materials used for their preparation were commercial products, which were redistilled until a fairly high degree of purity was obtained.

The *p*-chlorophenacyl bromide was the least difficult to prepare. It was found by experiment that for the best yield of *p*-chloro-acetophenone (of *p*-bromo- and *p*-iodo- also), the following proportions of materials are to be used: one mole of monochlorobenzene, or 112 g. (157 g. of bromobenzene, or 204 g. of iodobenzene), 85 g. of acetyl chloride (10% excess), 150 g. of anhydrous aluminum chloride (10% excess) and 250 g. of carbon disulfide as solvent. The chlorobenzene, aluminum chloride and carbon disulfide were put in a balloon flask fitted with a reflux condenser. The acetyl chloride was added through the condenser in 5 g. portions at intervals of about half an hour. In order to start the reaction it was necessary to immerse the flask in warm water for a short time, after which the reacting mixture was cooled with tap water, so that a slow evolution of hydrochloric acid occurred. If the temperature is kept low the formation of gummy products is almost entirely avoided. After the reaction was completed, *i. e.*, when the evolution of hydrochloric acid ceased, the mixture was heated on a water bath at 70–80° in order to drive off the carbon disulfide. The product was then decomposed gradually with ice water (or cracked ice). The *p*-chloro-acetophenone separated as a heavy, yellow oil, which was dried and distilled under reduced pressure. The distillate was redistilled at atmospheric pressure, the portion going over between 230° and 240° being kept. Gautier[1] gives the boiling point as 232°.

The *p*-chloro-acetophenone, dissolved in glacial acetic acid (about 50 g. in 100 cc.) was treated with one molecule of bromine, the latter being added slowly in order to keep the temperature of the reacting mixture from rising too high. A slow, constant evolution of hydrobromic acid is desirable. The *p*-chlorophenacyl bromide separated in yellow crystals as it was formed.

Upon completion of the bromination the mixture was cooled to 0° and the crystals collected on a filter. To separate them further from any oily material the crystals were centrifuged. The crude product was then dissolved in the least amount of 95% alcohol possible and boiled a few minutes with a mixture of animal and prepared wood charcoal. The saturated solution was then filtered quickly through a hot filter, the *p*-chlorophenacyl bromide separating on cooling as fine, white crystals.

[1] *Ann. chim. phys.*, [6] **14**, 373 (1888).

Only one recrystallization of the crude product was necessary to give the pure reagent melting at 96.5°.

The *p*-bromophenacyl bromide was made similarly. Instead of obtaining an oil in the first reaction, however, the *p*-bromo-acetophenone separated as a solid melting at 50.5°. The melting point of this compound, as determined by Schweitzer,[1] is 51°. Upon bromination, as above, *p*-bromophenacyl bromide was obtained as brownish yellow crystals, which required 3 recrystallizations from 95% alcohol before giving fine, white crystals melting constant at 109.7°.

Similar methods were used in the preparation of the *p*-iodophenacyl bromide. There seems to be some doubt in the literature as to the exact melting point of *p*-iodo-acetophenone. Klingel[2] made this compound from *p*-amido-acetophenone by the diazo-reaction, and obtained a product melting at 79°. Later Schweitzer,[3] using the Friedel and Craft reaction, prepared a compound melting at 85°. Schweitzer did not determine the position of groups in his compound, but assumed that, since the analogous method of preparation gave a *p*-chloro- and *p*-bromo-acetophenones, that his product was *p*-iodo-acetophenone. The compound obtained in this laboratory was a dark brown mass, which, when centrifuged and recrystallized from 95% alcohol, gave fine, yellow crystals melting at 83.5°. Some of the purified material was dissolved in glacial acetic acid and heated with a slight excess of chromic acid. The oxidation product was precipitated by the addition of water, filtered, washed and dried. It melted at 265°. The dry product was then dissolved in sodium carbonate solution and precipitated by dil. sulfuric acid. The compound again melted at 265°. The melting point of *p*-iodobenzoic acid is given as 265–6°. This shows that the $-COCH_3$ group enters the *para* position and that the compound is actually *p*-iodo-acetophenone.

The *p*-iodo-acetophenone was then brominated, as above. After 5 recrystallizations from 95% alcohol, *p*-iodophenacyl bromide was obtained as fine, slightly yellow crystals melting at 113.5°. Small portions of the product were recrystallized from carbon disulfide, ether and benzene, and in all cases white crystals, turning yellow in the air and melting at 113.5°, were obtained. The *p*-iodophenacyl bromide on analysis gave

Calc.: I, 39.06; Br, 24.59. Found: I, 38.90; Br, 24.57.

The bromination of the halogen acetophenones may be carried out in carbon disulfide also, but much better results are obtained with glacial acetic acid as a medium.

No special attempt was made to obtain the very best yields of final products, the main object being a fairly high degree of purity. The yields

[1] *Ber.*, 24, 550 (1891).
[2] *Ibid.*, 18, 2692 (1885).
[3] *Ibid.*, 24, 551 (1891).

(calculating from the amount of phenyl halide used) of crude products in the case of the *p*-chlorophenacyl bromide were 78–82% (80–85% yield of the *p*-chloro-acetophenone in the first stage and 94–96% of the *p*-chloro-acetophenone converted to *p*-chlorophenacyl bromide in the second stage), of the *p*-bromo compound 70–75% (70–80% yield in the first stage and 90–95% yield in the second stage), and of the *p*-iodo compound 55–60% (50–60% yield in the first stage and 90–95% yield in the second stage).

Method of Work.

The method of preparation of the esters was similar to that used in previous work[1] on the identification of acids. In the case of the *p*-chlorophenacyl esters 0.84 g. of reagent was used, of the *p*-bromo esters one g., and of the *p*-iodo esters 0.58 g., equivalent to 0.5 g. of the *p*-bromo, the smaller quantity being used on account of lower solubility. In a few cases where the degree of solubility of the esters could be predicted, *i. e.*, extremely soluble or difficultly soluble, more or less of the reagent was used as desired. For the addition of solvent, the calculation of the percentage composition of solvent and the filtration and washing of precipitates, the method of procedure adopted by Rather and Reid (*q. v.*), was followed. Monobasic acids were heated on the water bath for one hour, except acetic, propionic, glycolic and lactic which were heated only from $^1/_2$ to $^3/_4$ hour, dibasic acids were heated 2 hours and tribasic 3 hours. The precipitation of the esters was brought about by immersion of the flask in tap-water, except in a few cases where it was necessary to cool to 0° in order to start crystallization. The reagents and acids were weighed to 0.01 g. and the alcohol and water measured from pipets. Where it was possible to obtain them the alkali salts of the acids were used, otherwise the free acid was not quite neutralized with sodium carbonate in the reaction flask just before the reagent and alcohol were added. In the case of stearic, palmitic and margaric acids a solution of sodium alcoholate, containing the required amount of base, was added to the acid and warmed until the sodium salt of the acid precipitated on cooling. The reagent and solvent were then added and the ordinary procedure followed.

Recrystallization of the esters was carried out until a constant melting point was obtained. The melting points were taken in a small beaker containing conc. sulfuric acid which was well stirred. The same thermometer was used throughout, no corrections being applied. The thermometer registered correctly at 0° and 0.1° too low at 100°, while the melting point of pure benzoic acid taken under the conditions used was 121.5° as compared with the correct melting point of 121.25°.

[1] THIS JOURNAL, 39, 124, 701 and 1727 (1917); 41, 75 (1919).

The solubilities given for the esters are only approximate. The solubilities in the tables below were determined for the boiling alcoholic solution of the percentage composition expressed under "% Solvent" and for the solution cooled to about 20–25°.

Results.

The results of the investigation are given in the following tables in the form used by Rather and Reid (*q. v.*). Table I contains the *p*-chlorophenacyl esters, Table II the *p*-bromophenacyl esters and Table III the *p*-iodophenacyl esters. The first line represents the original preparation and the following lines each succeeding crystallization. The first crop is the quantity of ester precipitated on cooling the alcoholic solution of the percentage composition stated. The second crop is the quantity of ester held in solution at 20–25° and precipitated by dilution with water.

TABLE I.

p-Chlorophenacyl Esters.

Acids.	Solvent. %	Solvent. Cc.	First crop. Wt.	First crop. M. p. °C.	Second crop. Wt.	Second crop. M. p. °C.	% yield of ester.	Cc. solvent to dissolve 1 g. of ester. Hot.	Cc. solvent to dissolve 1 g. of ester. Cold.
Acetic CH_3COOH	47	20	0.46	65.6	0.14	62.8	78	...	....
	31	30	0.35	66.8	trace	....	....	65	280
	31	22	0.26	67.2	trace	66	....	...	....
	31	15	0.20	67.2	trace	....	....	...	....
Aconitic $C_3H_3(COOH)_3$	76	25	0.33	167.4	emulsion		44	...	....
	95	50	0.08[a]	168.8	0.17[b]	168.8	....	315	650
	95	50	0.06[c]	169	....	....	....	...	....
Benzoic C_6H_5COOH	63	60	0.75	118.5	0.15	115	91	...	....
	57	33	0.71	118.6	0.02	118.6	....	44	870
Ethyl-glycolic $C_2H_5OCH_2COOH$	63	15	0.59	94.4	0.20	80	86	...	....
	27	35	0.54	94.4	....	....	....	60	700
Succinic $(CH_2COOH)_2$	86	55	0.12	196	(0.44)	(95.5)	16	...	....
	95	60	0.05[a]	197.5	0.05[b]	197.2	....	800	2500
Thiocyanic HCNS	76	25	0.58	135.2	0.15	124	95.5	...	....
	55	24	0.48	135.2	0.05	133.5	....	41	250
Tricarballylic $C_3H_5(COOH)_3$	81	35	0.39	124	....	....	52	...	....
	95	50	0.27[a]	125.6	0.06[b]	126	....	150	800
	95	40	0.25	125.6	....	....	....	...	....

[a] Portion of 1st 1st dissolved by 50 cc. of 95% EtOH.

[b] Portion undissolved.

[c] Portion of *b* dissolved by 50 cc. of 95% EtOH.

Another preparation gave a yield of 90% and melted at 118.6°.

[a] Portion of 1st 1st dissolved by 60 cc. of 95% EtOH.

[b] Portion undissolved.

[a] Portion of 1st 1st dissolved by 50 cc. of 95% EtOH.

[b] Portion undissolved.

TABLE II.

p-Bromophenacyl Esters.

Acids.	Solvent. %	Solvent. Cc.	First crop. Wt.	First crop. M. p. ° C.	Second crop. Wt.	Second crop. M. p. ° C.	% yield of ester.	Cc. solvent to dissolve 1 g. of ester. Hot.	Cc. solvent to dissolve 1 g. of ester. Cold.
Acetic CH_3COOH	60	16	0.55	84.5	0.25	82.5	86.5	...	....
	40	14	0.48	85	0.01	82.8	....	27	210
	40	14	0.41	85	0.03	83.8	....	...	....
Aconitic $C_3H_3(COOH)_3$	79	36	0.41	184	oil	...	45	...	....
	95	70	0.03[a]	184	0.28[b]	186	....	540	....
	95	50	0.01[c]	186	0.23[d]	185.5	....	...	....

The ester precipitated almost entirely from the hot solution.

[a] Portion dissolved by 70 cc. of 95% EtOH.

[b] Portion undissolved.

[c] Portion of (*b*) dissolved by 50 cc. of 95% EtOH.

[d] Portion of (*b*) undissolved.

Anisic p-$CH_3OC_6H_4COOH$	86	55	1.17	152	trace	...	93.5	...	....
	95	80	1.05	152	0.06	152	....	68	625
Benzoic C_6H_5COOH	63	30	0.69	119	0.04	110	85	...	....
	64	22	0.64	119	0.03	118.2	....	31	470

Another preparation gave a yield of 92% and melted at 119°.

Butyric, normal $CH_3CH_2CH_2COOH$	63	18	0.62	63	0.23	60.8	83.5	...	....
	61	14	0.48	63.2	0.11	63	....	22	110
	61	14	0.36	63.2	0.11	62.5	....	...	....
Butyric, iso. $(CH_3)_2CHCOOH$	63	18	0.72	76.2	0.23	74	93	...	....
	67	17	0.55	76.8	0.14	75	....	23	95
	46	25	0.51	76.8	0.01	74	....	...	....
Capric $CH_3(CH_2)_8COOH$	76	25	1.12	66	0.05	50	87.5	...	....
	80	26	0.99	66	...	65	....	23	215
Caproic $CH_3(CH_2)_4COOH$	67	17	0.92	71	0.06	66	88	...	....
	61	43	0.76	71.6	...	70.5	....	46	270
	62	35	0.65	71.6	...	71	....	...	....
Caprylic $CH_3(CH_2)_6COOH$	71	40	0.97	65	0.13	60	90	...	....
	63	45	0.87	65.5	0.08	63	....	46	450
	65	41	0.79	65.5	0.07	64	....	...	....
Cinnamic $C_6H_5CH:CHCOOH$	66	100	0.81	146	...	...	80	...	....
	73	67	0.79	145.6	...	...	....	82	2700
	73	65	0.75	145.6	...	...	....	...	....
Citric $HOC_3H_4(COOH)_3$	87	60	0.38	148	...	...	40.5	...	....
	95	85	0.34	148	...	...	....	220	1850

If the solution is cooled too rapidly, the ester separates as a gum.

Erucic $C_8H_{17}CH:(CHCH_2)_{11}$-COOH	84	54	1.74	61	0.16	51	90.5	...	....
	88	44	1.62	61	...	...	....	25	360
Ethyl-glycolic $C_2H_5OCH_2COOH$	54	35	0.79	104.8	0.14	90	85	...	....
	47	28	0.71	104.8	...	...	....	35	360

TABLE II (*continued*).

Acids.	Solvent. %	Solvent. Cc.	First crop. Wt.	First crop. M. p. ° C.	Second crop. Wt.	Second crop. M. p. ° C.	% yield of ester.	Cc. solvent to dissolve 1 g. of ester. Hot.	Cc. solvent to dissolve 1 g. of ester. Cold.
Glycolic $OHCH_2COOH$	47	20	0.71	134.6	0.09	121	81	...	....
	23	40	0.61	133	...	...	....	...	....
	47	20	0.45	136	...	123.5	....	32	125
	47	14	0.36	138	...	...	....	...	....
	47	10	0.31	138	...	...	....	...	....
Hippuric $C_6H_5CONHCH_2COOH$	76	25	1.06	150	0.15	130	89	...	....
	52	45	1.00	151	0.03	151	....	42	750
	50	42	0.94	151	...	...	....	...	....
Hydrocinnamic $C_6H_5CH_2CH_2COOH$	76	25	1.19	104	0.05	102	95.5	...	....
	67	35	1.14	104	0.02	103.5	....	30	625
i. Lactic $CH_3CHOHCOOH$	63	18	0.19	112.8	0.58	111	74	...	....
	21	58	0.59	112	...	...	....	...	....
	19	25	0.50	112.8	0.02	112.2	....	42	280
	19	21	0.42	112.8	...	...	....	...	....
	The 1st 1st and 1st 2nd crops were added, together and dissolved in 58 cc. of 21% alcohol, the 0.59 g. of ester precipitating being called 2nd 1st crop.								
Laevulinic $CH_3CO(CH_2)_2COOH$	63	15	0.74	84	0.24	82	86.5	...	....
	36	65	0.58	84	0.06	84	....	90	425
	39	50	0.47	84	0.05	84	....	...	....
Margaric $CH_3(CH_2)_{15}COOH$	95	30	1.41	78.2	gum	...	84	...	....
	91	52	1.18	78.2	...	76	....	36	225
Palmitic $CH_3(CH_2)_{14}COOH$	95	30	1.41	81.5	gum	...	86.5	...	....
	83	34	1.18	81.5	...	80.8	....	24	150
Phenylacetic $C_6H_5CH_2COOH$	76	25	0.62	88.6	0.22	87	94	...	....
	68	18	0.48	89	0.03	86	....	30	130
	76	20	0.26	89	0.17	88.8	....	...	....
Propionic CH_3CH_2COOH	63	15	0.56	58.8	0.36	55.5	94	...	....
	41	25	0.47	59	0.05	59	....	44	300
	47	20	0.35	59	...	...	....	...	....
Pyromucic C_4H_3OCOOH	76	25	0.98	138.5	0.07	115	88	...	....
	67	28	0.90	138.5	0.03	138.5	....	28	350
Salicylic o-OHC_6H_4COOH	76	25	0.88	140	(0.2)	(101)	73	...	....
	67	62	0.85	140	0.01	138	....	70	2700
Sebacic $COOH(CH_2)_8COOH$	76	25	0.90	142	0.18	112	75	...	....
	95	80	0.29[a]	147	0.55[b]	147	....	230	1350
	95	60	0.26[c]	147	...	...	....	...	....
Sorbic $CH_3(CH:CH)_2COOH$	76	25	0.95	129	0.04	128.2	89	...	....
	63	45	0.91	129	0.02	128.6	....	47	1200
Stearic $CH_3(CH_2)_{16}COOH$	95	42	1.30	78	0.15	78	84	...	....
	87	65	1.14	78.5	...	78.5	....	50	410

[a] Portion of 1st 1st dissolved by 80 cc. of 95% EtOH.

[b] Portion undissolved.

[c] Portion of [a] dissolved in 60 cc. of 95% EtOH.

TABLE II (*continued*).

Acids.	Solvent. %.	Solvent. Cc.	First crop. Wt.	First crop. M. p. ° C.	Second crop. Wt	Second crop. M. p. ° C.	% yield of ester.	Cc. solvent to dissolve 1 g. of ester. Hot.	Cc. solvent to dissolve 1 g. of ester. Cold.
Succinic $(CH_2COOH)_2$	86	55	0.44	210	(0.29)	(105)	47.5	...	....
	95	60	0.01[a]	211	0.39[b]	211	....	1200	....
	95	60	0.01[c]	211	0.35[d]	211	....	...	....
Thiocyanic HCNS	80	38	0.73	147.5	0.14	132	94	...	....
	80	30	0.60	146.5	0.10	145	....	41	240
	60	32	0.53	146.5	0.05	145	....	...	....
o-Toluic o-$CH_3C_6H_4COOH$	76	25	0.51	58	(0.27)	(62.5)	57	...	....
	54	35	0.45	56.9	emulsion	...	....	68	550
	65	41	0.24	56.9	...	...	....	...	....
m-Toluic m-$CH_3C_6H_4COOH$	71	40	0.75	108.5	emulsion	...	84	...	....
	65	32	0.69	108	emulsion	...	....	42	500
	65	29	0.65	108	emulsion	...	....	...	....
p-Toluic p-$CH_3C_6H_4COOH$	81	35	0.79	153	trace	...	88	...	....
	79	60	0.74	153	trace	152.5	....	76	1100
Tricarballylic $C_3H_5(COOH)_3$	81	35	0.69	137.6	oil	...	76	...	....
	95	105	0.50[a]	138.2	0.11[b]	137.8	....	180	1330
	95	90	0.42[c]	138.2	...	138	....	...	....
Valeric, normal. $CH_3(CH_2)_3COOH$	63	18	0.84	63.6	0.14	58	91	...	....
	67	21	0.61	63.6	0.20	62.5	....	25	100
Valeric, iso $(CH_3)_2CHCH_2COOH$	66	20	0.51	65	0.39	51.5	84	...	....
	66	20	0.41	67	0.03	59	84	...	....
	0.37 g. of 2nd 1st taken and dissolved in 33 cc. of 40% alcohol.								
	40	33	0.33	68	0.01	67	90	90	730
	41	23	0.31	68	.....	...	....	...	....

[a] Portion of 1st 1st dissolved by 60 cc. of 95% EtOH.
[b] Portion undissolved.
[c] Portion of B dissolved by 60 cc. of 95% EtOH.
[d] Portion of B undissolved.

The *p*-chloro- and *p*-bromo-thiocyanates are pale yellowish green in color, the only colored esters obtained.

[a] Portion of 1st 1st dissolved by 105 cc. of 95% EtOH.
[b] Portion undissolved.
[c] Portion of [a] dissolved by 90 cc. of 95% EtOH.

Another preparation melted at 68°.

Esters Unsuitable for Identification.

The *p*-bromophenacyl esters of asparaginic, maleic, racemic and tartaric acids were obtained in small quantities, but were very difficultly soluble in boiling 95% alcohol. These esters did not melt, but decomposed on heating and hence are of no value for identification purposes. The *p*-bromophenacyl ester of mucic acid was obtained in a minute quantity, insufficient to recrystallize. It decomposed at 215–225°. It was thought that the *p*-chlorophenacyl esters of the above acids would melt,

TABLE III.

p-Iodophenacyl Esters.

Acids.	Solvent. %.	Solvent. Cc.	First crop. Wt.	First crop. M. p. ° C.	Second crop. Wt.	Second crop. M. p. ° C.	% yield of ester.	Cc. solvent to dissolve 1 g. of ester. Hot.	Cc. solvent to dissolve 1 g. of ester. Cold.
Acetic CH_3COOH	63	30	0.57	113	0.16	110	90	...	....
	59	32	0.38	114	0.14	113.2	..	56	170
	59	21	0.26	114	0.09	113.5	..	...	....
Benzoic C_6H_5COOH	81	35	0.46	126.5	0.11	123.5	86	...	....
	63	30	0.43	126.5	0.02	126	..	65	830
Butyric, normal $CH_3(CH_2)_2COOH$	71	40	0.48	80.8	0.56	78	87	...	....
	71	16	0.25	81.2	0.20	80.8	..	33	70
	63	15	0.12	81.4	0.10	81.4	..	...	....
Butyric, iso $(CH_3)_2CHCOOH$	63	24	0.75	109	0.11	102.5	95	...	....
	64	25	0.62	109.2	0.10	107	..	33	210
Capric $CH_3(CH_2)_8COOH$	76	31	0.63	80	0.03	77	88	...	....
	83	24	0.50	80	0.10	79.9	..	37	170
Caproic $CH_3(CH_2)_4COOH$	71	32	0.75	81.4	0.15	78	92	...	....
	72	34	0.58	81.5	0.14	80.6	..	45	200
Caprylic $CH_3(CH_2)_6COOH$	71	40	0.53	77	0.07	74	86	...	....
	82	22	0.34	76.8	0.15	75	..	41	110
	84	17	0.14	77	0.16	76.8	..	...	....
Erucic $C_8H_{17}CH:CH-(CH_2)_{11}COOH$	71	40	1.93	72.6	oil	...	92	...	....
	95	54	1.51	73.6	gum	...	..	28	130
	95	50	1.40	73.8	0.06	72.5	..	...	....
l. Lactic $CH_3CHOHCOOH$	58	26	0.55	138.8	0.18	134.5	81	...	....
	53	34	0.34	139.8	0.14	138.2	..	61	160
	51	22	0.24	139.8	0.07	139	..	...	....
Margaric $CH_3(CH_2)_{15}COOH$	95	30	0.61	89	gum	...	66	...	....
	95	30	0.48	88.8	trace	88.8	..	49	230
Palmitic $CH_3(CH_2)_{14}COOH$	95	30	0.69	90	gum	...	77	...	....
	90	21	0.66	90	trace	...	..	30	800
Propionic CH_3CH_2COOH	56	44	0.83	94.6	0.21	91	91	...	....
	67	17	0.61	94.9	0.18	93.6	..	20	75
	63	15	0.44	94.9	0.14	94.2	..	...	....
Stearic $CH_3(CH_2)_{16}COOH$	95	30	0.79	90.8	0.09	74	93	...	....
	91	26	0.77	90.5	trace	...	..	32	930
Valeric, normal $CH_3(CH_2)_3COOH$	71	20	0.43	76	0.11	72	87	...	....
	68	18	0.31	78.6	0.10	75	..	41	145
	68	14	0.22	78.6	0.07	77.9	..	...	....
Valeric, iso $(CH_3)_2CHCH_2COOH$	68	28	1.00	72	0.23	69.8	99	...	....
	63	30	0.75	78.8	0.20	71	..	30	120
	63	22	0.64	78.8	trace	71	..	...	....

Another preparation of normal valerate gave a yield of 92% and melted at 78.6°.

but the ester of asparaginic decomposed at 145–150° and that of racemic decomposed at 180–190°. It was, therefore, not considered worth while to try tartaric, maleic or mucic acids. The data in regard to the *p*-bromophenacyl esters of asparaginic, maleic, racemic and tartaric acids is given in Table IV.

TABLE IV.

p-Bromophenacyl Esters.

Acids.	Solvent. %	Solvent. Cc.	First. Wt.	First. Temp. of decomp. °C.	Second. Wt.	Second. Temp. of decomp. °C.	% yield of ester.	Cc. solvent to dissolve 1. g. of ester. Hot.	Cold.
Asparaginic	83	40	0.26	140–50	oil	....	22	...	....
$NH_2CO(NH)_2$-C_2H_3COOH	95	70	Ao.02	175–6	Bo.11	170	..	470	....
Maleic	80	36	0.24	190	(0.41)	(100)	27	...	....
HOOCCH : CHCOOH	95	60	Ao.03	168–70	Bo.10	225–30	..	420	900
Racemic	71	40	0.47	204–6	(0.16)	(108.8)	48	...	....
(OHCHCOOH)	95	70	Ao.11	204–6	Bo.32	205	..	460	1600
Tartaric	71	40	0.56	170	(0.16)	(109)	57	...	....
(OHCHCOOH)	95	60	Ao.04	210–15	Bo.44	215–6	..	490	....

In all the above cases A is portion of 1st 1st dissolved by 95% EtOH and B is the portion undissolved.

Acids Giving Negative Results.

These acids were tried with the *p*-bromo- and *p*-iodophenacyl bromides. Gallic acid gave a precipitate only in extremely dilute alcohol solutions. This was unsatisfactory as it was finely divided and difficult to filter and dry. It decomposed at 175–190° without a definite melting point.

The sodium salt of linoleic acid seemed to react with the reagents to a small extent only and the precipitates obtained with both reagents were saturated with an oil which could not be entirely removed. The melting points of both esters were about the same and kept slowly rising with each recrystallization, running from 66° to 78°.

Oleic acid behaved similarly with both reagents, the melting points of the supposed esters running from 53° to 63°.

It is possible that the small precipitate formed was the ester of some other fatty acid present as an impurity in the linoleic and oleic acids, and from which they could not be separated.

Oxalic, monochloro-acetic and trichloro-acetic acids did not react at all as the pure reagent was obtained from the solutions nearly quantitatively.

Formic acid in 2 cases did not react as the reagent was recovered pure. In one case a small amount of a precipitate was obtained, before the reagent separated, which softened and melted at 115–9°. Not enough of this was obtained with which to work, and further attempts gave none at all.

The only acid to give a liquid ester was α-oxybutyric. This was tried with both the *p*-bromo- and *p*-iodophenacyl bromides, but in both cases the esters remained oils at 0°.

Analysis of Esters.

Several esters were chosen at random and analyzed. The results are as follows:

Ester.	Analysis for	Calc. %	Found %
p-Bromophenacyl-*m*-toluate	Br	24.00	24.23
p-Bromophenacyl thiocyanate	Br	31.20	31.42
p-Chlorophenacyl benzoate	Cl	12.91	13.10
p-Bromophenacyl benzoate	Br	25.04	25.14
p-Iodophenacyl benzoate	I	34.66	34.88
p-Iodophenacyl norm. valerate	I	36.66	36.57

This seemed to indicate that the reagents were reacting in the way expected.

Comparison of *p*-Halogen Phenacyl Esters with Phenacyl and *p*-Nitrobenzyl Esters.

As can be seen, by comparing Tables I, II and III, the yields of *p*-chlorophenacyl esters are slightly lower than the yields of corresponding *p*-bromophenyl esters, and those of the *p*-bromo are lower than those of the *p*-iodophenacyl esters. The same relation holds for the melting points although the difference is more marked than in the case of the yields, the melting points of the *p*-chloro esters running about 10° lower than those of the *p*-bromo esters, and those of the *p*-bromo esters about 10° lower than those of the *p*-iodo esters.

For general purposes the *p*-bromophenacyl esters are more useful for identification than the *p*-chloro- or *p*-iodophenacyl esters. On comparing 18 of the *p*-bromophenacyl esters with the corresponding *p*-nitrobenzyl esters the yields in both cases average 80%, while the average melting point of the *p*-nitrobenzyl esters is 84.1° and of the *p*-bromophenacyl esters is 118.8°, giving 34.7° in favor of the latter.

Comparing the *p*-bromophenacyl esters with the corresponding phenacyl esters it is seen that although the average yield of the former is only 70% while that of the latter is 82%, the average melting point of the former is 130.7° against only 96.3° for the phenacyl esters.

In every case the *p*-bromophenacyl ester melted higher than the corresponding *p*-nitrobenzyl or phenacyl esters.

A further comparison of the value of the reagents shows that phenacyl bromide is particularly good in the case of the dibasic acids. *p*-Bromophenacyl bromide gave very poor results with dibasic acids, but for monobasic acids, especially those of the formic acid series, it gave better results than any other reagents thus far tried.

p-Halogen Phenacyl Alcohols.

Since the *p*-halogen phenacyl esters are derivatives of the corresponding alcohols, it was considered to be a matter of interest to prepare the latter. The method of preparation was similar to that used by O. Fischer[1] for benzoyl carbinol, and recommended by Straus for the *p*-chlorophenacyl alcohol, *i. e.*, the hydrolysis of the *p*-halogen phenacyl acetates in water containing a slight excess of barium carbonate. The following proportions of materials were used with good results: 2 g. of *p*-chlorophenacyl acetate, one g. of barium carbonate and 100 cc. of water; 2 g. of *p*-bromo-acetate, 0.8 g. of barium carbonate and 125 cc. of water; and 2 g. of *p*-iodoacetate, 0.7 g. of barium carbonate and 150 cc. of water. The acetate was put in an Erlenmeyer flask with the required amount of barium carbonate and water and refluxed for about one hour. The solution was filtered hot, the alcohol crystallizing out, upon cooling, in fine, white plates. The *p*-chlorophenacyl alcohol melted at 122.4°, when crystallized from water, ether and absolute alcohol, which checks well with Straus' observation of 122–3°. *p*-Bromophenacyl alcohol melted at 136.6° and *p*-iodophenacyl alcohol melted at 152°. The alcohols are very soluble in ether, hot water and hot alcohol, crystallizing well from the latter. Analyses of the *p*-bromo and *p*-iodo alcohols gave the following results:

Calc. for *p*-bromophenacyl alcohol: Br, 37.16. Found: 36.98.
Calc. for *p*-iodophenacyl alcohol: I, 48.43. Found: 48.24.

The analyses and melting points (crystallization from water, ether and alcohol giving identical melting points) also indicate that the alcohols contain no water of crystallization. No analysis of the *p*-chlorophenacyl alcohol was made, as it was evident that it was identical with the compound prepared by Straus, who analyzed his product.

Summary.

The *p*-halogen phenacyl bromides, particularly *p*-bromophenacyl bromide, serve as useful reagents for the identification of acids, especially monobasic aliphatic acids. They are easily prepared and react readily with the alkali salts of the acids when boiled in dil. alcohol solutions. The range of the melting points of the esters is very convenient for identification purposes.

The following esters have been prepared and studied:

p-Chlorophenacyl Esters.

	M. p. °C.		M. p. °C.
Acetate	67.2	Succinate	197.5
Aconitate	169.0	Thiocyanate	135.2
Benzoate	118.6	Tricarballylate	125.6
Ethyl-glycolate	94.4		

[1] *Ber.*, 24, 2680 (1891).

p-Bromophenacyl Esters.

	M. p. °C.		M. p. °C.
Acetate	85.0	Laevulinate	84.0
Aconitate	186.0	Margarate	78.2
Anisate	152.0	Palmitate	81.5
Benzoate	119.0	Phenyl-acetate	89.0
Butyrate	63.2	Propionate	59.0
Iso-butyrate	76.8	Pyromucate	138.5
Caprate	66.0	Salicylate	140.0
Caproate	71.6	Sebacate	147.0
Caprylate	65.5	Sorbate	129.0
Cinnamate	145.6	Stearate	78.5
Citrate	148.0	Succinate	211.0
Erucate	61.0	Thiocyanate	146.5
Ethyl-glycolate	104.8	*o*-Toluate	56.9
Glycolate	138.0	*m*-Toluate	108.0
Hippurate	151.0	*p*-Toluate	153.0
Hydrocinnamate	104.0	Tricarballylate	138.2
Lactate	112.8	Valerate	63.6
		Isovalerate	68.0

p-Iodophenacyl Esters.

	M. p. °C.		M. p. °C.
Acetate	114.0	Erucate	73.8
Benzoate	126.5	Lactate	139.8
Butyrate	81.4	Margarate	88.8
Iso-butyrate	109.2	Palmitate	90.0
Caprate	80.0	Propionate	94.9
Caproate	81.5	Stearate	90.5
Caprylate	77.0	Valerate	78.6
Iso-valerate	78.8		

BALTIMORE, MARYLAND.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF TUFTS COLLEGE.]

THE ADDITION OF 1,3-DIKETONES TO ISOTHIOCYANATES. I. ACETYLACETONE AND CERTAIN ARYL ISOTHIOCYANATES.

BY DAVID E. WORRALL.

Received March 1, 1920.

The β-diketones are characterized by several reactions that make them of particular value for synthetic purposes. They react with hydroxylamine and with phenylhydrazine to form mono-substituted derivatives; but, through the loss of a molecule of water, these rearrange to form isoxazols and pyrazols, reactions that illustrate the ease with which 5-membered ring compounds may be closed. The presence of an acidic methylene group makes possible the formation of metal derivatives; hence these diketones are capable of transformations similar to those so well known with malonic ester.